

Soft X-Ray Photoemission Studies of Hf Oxidation

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Abstract

Soft X-Ray Photoemission Spectroscopy using surface sensitive Synchrotron Radiation has been applied to accurately determine the binding energy shifts and the valance band offset of the HfO₂ grown on Hf metal. Charging of oxide films under x-rays (or other irradiation) is circumvented by controlled and sequential in-situ oxidation. Photoemission results show the presence of metallic Hf (from the substrate) with the 4f_{7/2} binding energy of 14.22 eV, fully oxidized Hf (from HfO₂) with the 4f_{7/2} binding energy of 18.16 eV, and at least one clear suboxide peak. The position of the valence band of HfO₂ with respect to the Hf(m) Fermi level is determined as 4.05 eV.

Introduction

Although photoelectron spectroscopy is widely used for elucidating the electronic structure of numerous materials, interfaces, and surfaces, systematic studies of hafnium and its oxides are scarce¹⁻³. Sarma et. al. employed X-ray photoelectron spectroscopy to investigate oxides of second- and third-row transition metals, including those of rare earths¹. They described the spin-orbit splittings and the binding energies of core levels of the metals. It was shown that the core-level binding energies increased with the oxidation state of the metal atom. Specific features of individual oxides concerning satellites,

multiplet structure, configuration mixing, and other properties, were also discussed and a binding energy of 29.8 and 16.4 eV were assigned to the $5p_{3/2}$ and $4f_{7/2}$ levels of HfO_2 respectively. Nyholm et. al. reported the binding energies of all core levels in the N and O shells for the elements from hafnium to bismuth (that are accessible with Al $K\alpha$ radiation) using X-ray photoelectron spectroscopy². They reported binding energies of 29.9 and 14.23 eV for the metallic $5p_{3/2}$ and $4f_{7/2}$ levels of Hf as referenced to Au $4f_{7/2}$ level (84.00 eV). The Handbook of X-ray Photoelectron Spectroscopy gives the binding energies of the Hf $4f_{7/2}$ as 14.4 and 16.7 eV for the Hf(m) and HfO_2 respectively³. Morant et. al. were the first to report on a systematic XPS investigation of the initial stages of oxidation of hafnium⁴, where they studied the oxidation kinetics of polycrystalline hafnium at room temperature under low oxygen pressures ($\sim 10^{-7}$ torr). They reported that suboxides are formed in the early stages, and that HfO_2 formation proceeded through oxidation of suboxides. The film thickness saturates to a value of 12 Å (under their conditions) with an average Hf:O stoichiometry of 1:1.8. They also reported 14.31 and 18.13 eV binding energies for the Hf $4f_{7/2}$ levels of the metallic Hf and the HfO_2 respectively. As can be deduced from these studies, although the reported binding energies for Hf(m) are in agreement with each other, those for the HfO_2 have a large scatter (as much as 1.7 eV).

Interest in hafnium dioxide has grown enormously since 1998 because of its promise for use as a high-k dielectric in future highly scaled memory and logic MOSFET devices⁵⁻⁹. As a result, extensive use of XPS and other surface techniques have recently been reported on hafnium oxide and related systems^{6-8,10-12}. Although HfO_2 has a moderately high dielectric constant and band gap (both useful for ultrathin dielectric

applications in micro- or nano-electronics), charging during photon or electron irradiation can make it difficult to determine the binding energies and/or the chemical states accurately. This, in turn, may lead to incorrect assignments and conclusions. For example, the binding energy of the Hf 4f_{7/2} levels of a thick film HfO₂ can be estimated as 17.3 and 17.4 eV from the recently published data of Ref. 7 (Figure 6) and Ref. 8 (Figure 3) respectively, again differing about 1 eV from the previously reported values. Furthermore, additional confusion may arise from incorrect assignment of the surface and the bulk states

In this letter, we present results from an investigation of the stepwise oxidation of polycrystalline hafnium foil using high-resolution (and surface sensitive) soft x-ray photoemission to accurately determine the binding energies, electronic states and valance band offsets of the oxide/metal system in order to clarify assignments.

Experimental

Polycrystalline hafnium foil (0.025mm thick) with a 3% Zr nominal content (Alfa Aesar) was used in this work. After cleaning with acetone and alcohol the foil was placed into the sample holder and loaded into the UHV chamber (base pressure 1×10^{-10} torr) for in-situ cleaning and controlled oxidation. Cleaning was accomplished in UHV by resistive heating of the foil. Controlled and stepwise oxidation was also accomplished in the UHV chamber by heating the foil to ca. 200°C and exposing it to 1×10^{-5} torr oxygen for various durations. Soft x-ray photoemission spectroscopy has been performed with monochromatic radiation at; i) the U8B beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory in the 120-400 eV range, and ii) the

9.3 beamline of the Advanced Light Source (ALS) at Lawrence Berkeley Laboratory in the 70-400 eV range.

Results and Discussion

The spectral features of the Hf foil immediately after introduction into UHV are presented in Figure 1. The spectra clearly indicate the presence of a “native” oxide (Fig1a) and only after in-situ cleaning do features belonging to the metal emerge (see Fig. 1b). The deconvolution of the Hf 4f spin-orbit couple is done after a Shirley background subtraction with the theoretical area ratio (3:4) held constant. The binding energy of the Hf 4f_{7/2} feature is reported as referenced to the Fermi energy of the cleaned hafnium foil. The Fermi energy is modeled by a Boltzmann broadened step function and the inflection point is found by fitting this function to the experimental data using a standard least-squares fitting method. As shown in the inset of Figure 1, the Hf 4f region can be fit to 4 spin-orbit doublets, each with 1.66 eV separation, with the corresponding 4f_{7/2} binding energies at 14.22, 14.58, 15.41, and 18.16 eV. The first two doublets have relatively narrow line-widths (~0.4 eV) and can be assigned to the Hf⁰(bulk-metal) and to the Hf⁰(surface-metal). The energy separation between the 4f_{7/2} levels of the bulk and surface metal (surface core level shift) was 0.36 eV, in good agreement single crystal¹³ and polycrystalline¹⁴ studies, the latter reporting a shift of 0.42 eV. The difference in core-level binding energies for the bulk and surface metal atoms results from a narrowing of the d-bands at the surface; the narrowing requires a charge transfer to align the Fermi level. For transition metals with d-bands less than half full such as Hf, the surface core-levels are shifted to larger binding energies since the surface acquires positive charge¹⁵.

The last two doublets exhibit larger widths (>0.9 eV) and can accordingly be assigned to a suboxide $\text{Hf}^{\text{X}+}$, and the fully oxidized hafnium Hf^{4+} . The 1.19 and 3.94 eV chemical shifts for the suboxide and the full oxide are in qualitative agreement with the previously reported XPS values of 0.90 and 3.64 eV respectively⁴. Similarly, the chemical shift in the binding energy of the $\text{Hf}5\text{p}_{3/2}$ level is determined as 3.9 eV exactly the same (within our experimental uncertainty) as the $4\text{f}_{7/2}$ shift.

Figure 2 presents the spectra of hafnium foil in the presence of the native oxide at different photon energies in the range of 70-130 eV. The use of synchrotron radiation with variable photon energy enables an assignment of the bands (for example O2p versus $\text{Hf}5\text{d}$, 6s mid-gap bands) as shown in Figure 2. As the photon energy increases (increasing the escape depth of electrons), there is a decrease in intensity in the 0-4 eV range, indicating that the valence band of the metal is mainly composed of $\text{Hf} 5\text{d}$ and 6s bands. The band in the range of 4.5-10 eV is mainly composed of O2p-like nonbonding π -orbitals with some contribution from $\text{Hf}5\text{d}$ levels. It is worth noting that the shoulder at around ~ 7.5 eV becomes more pronounced with increasing photon energy.

When the thickness of the oxide layer is increased (>20 nm), the sample undergoes extensive charging resulting in a significant shift to lower kinetic (higher binding) energies, which varies with flux and/or time. Figure 3-a shows the photon induced charging shifts that result when scans are taken consecutively with two-minute intervals. Under our conditions, we observed shifts on the order of 2 eV in the spectral features due to charging. The charging can be dissipated much faster upon annealing (after a 3s brief anneal to $\sim 200^\circ\text{C}$ the charging disappears, as shown in Figure 3-b). Therefore special care should be paid when analyzing thicker oxides.

The spectra corresponding to different O₂ exposures are given in the left panel of Figure 4. As the oxygen exposure increased, the intensity in the valence band region decreases (0-4 eV) and the band corresponding to O2p-like levels (4-10 eV) increases in intensity. The right panel presents the spectra of the fully oxidized sample in the energy range of 120-240 eV. This data set depicts the excitation energy dependence of the valence band cross-section. The cross-section of the valence band decreases as excitation energy increases as noted above. By sequentially oxidizing the sample, spectra can be obtained free from any charging effects. Hence stepwise and controlled oxidation is found to be a solution to accurately determine the chemical shift(s), valence-band offset(s), etc. of the oxide/metal system, as depicted in Figure 4.

The position of the valence band maximum with respect to the Fermi level is determined by using two different methods. One method employs a best straight line fit to represent the decay in valence band photoemission and the point of intersection of this line with the baseline is taken to be the valence band edge. The second method defines the edge as the point where the photoemission signal rises above the background by a certain percentage. In the inset of Fig. 4, the result of the fitting using the two methods are given, showing valence band offsets of 4.05 and ? eV respectively. This is the first report on the position of the valence band with respect to the Fermi level to the best of the authors' knowledge.

Conclusion:

Charging of oxide films under x-rays (or other irradiation) is an important issue that must be taken into consideration for precise electronic structure determination such

as core-level binding energies as well as valence band offsets. Measurements were taken as a function of time, thickness, and annealing condition. One solution to circumvent the charging problem, as presented in this contribution, is to perform a controlled and sequential oxidation. Photoemission results show the presence of metallic Hf (from the substrate) with the $4f_{7/2}$ binding energy of 14.22 eV, fully oxidized Hf (from HfO_2) with the $4f_{7/2}$ binding energy of 18.16 eV, and at least one clear suboxide peak. The Hf $5p_{3/2}$ chemical shift is exactly the same as that of $4f_{7/2}$. The position of the valence band of HfO_2 with respect to the Hf(m) Fermi level is determined as 4.05 eV.

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Table I. Binding energies (in eV) together with their FWHM (in eV) and assignments of the peaks of clean and oxidized polycrystalline Hf foil.

	VB onset	4f _{7/2}	5p _{3/2}
Hf ⁰ (metal, bulk)	0.00	14.22 (0.37)	29.9
Hf ⁰ (metal, surface)	-	14.58 (0.40)	-
Hf ^{x+} O _y (suboxide)	-	15.41 (0.97)	-
Hf ⁴⁺ O ₂	4.05	18.16 (0.92)	33.8

Figure Captions

Figure 1- Valence Band, 4f and 5p Photoemission Spectrum of polycrystalline Hf foil recorded at 100 eV photon energy before (a and a') and after (b and b') in-situ heating. The figure also contains the deconvoluted 4f region.

Figure 2- Spectra of the VB and 4f region of heated sample using different photon energies.

Figure 3- Single scans of the Hf4f region of a >20 nm thick oxide sample recorded consecutively (a) and with a brief (ca. 10 s) anneal between each scan.

Figure 4- Spectra recorded at 160 eV photon energy of during the stepwise oxidation of the Hf foil (a), and of the fully oxidized sample at different photon energies (b).

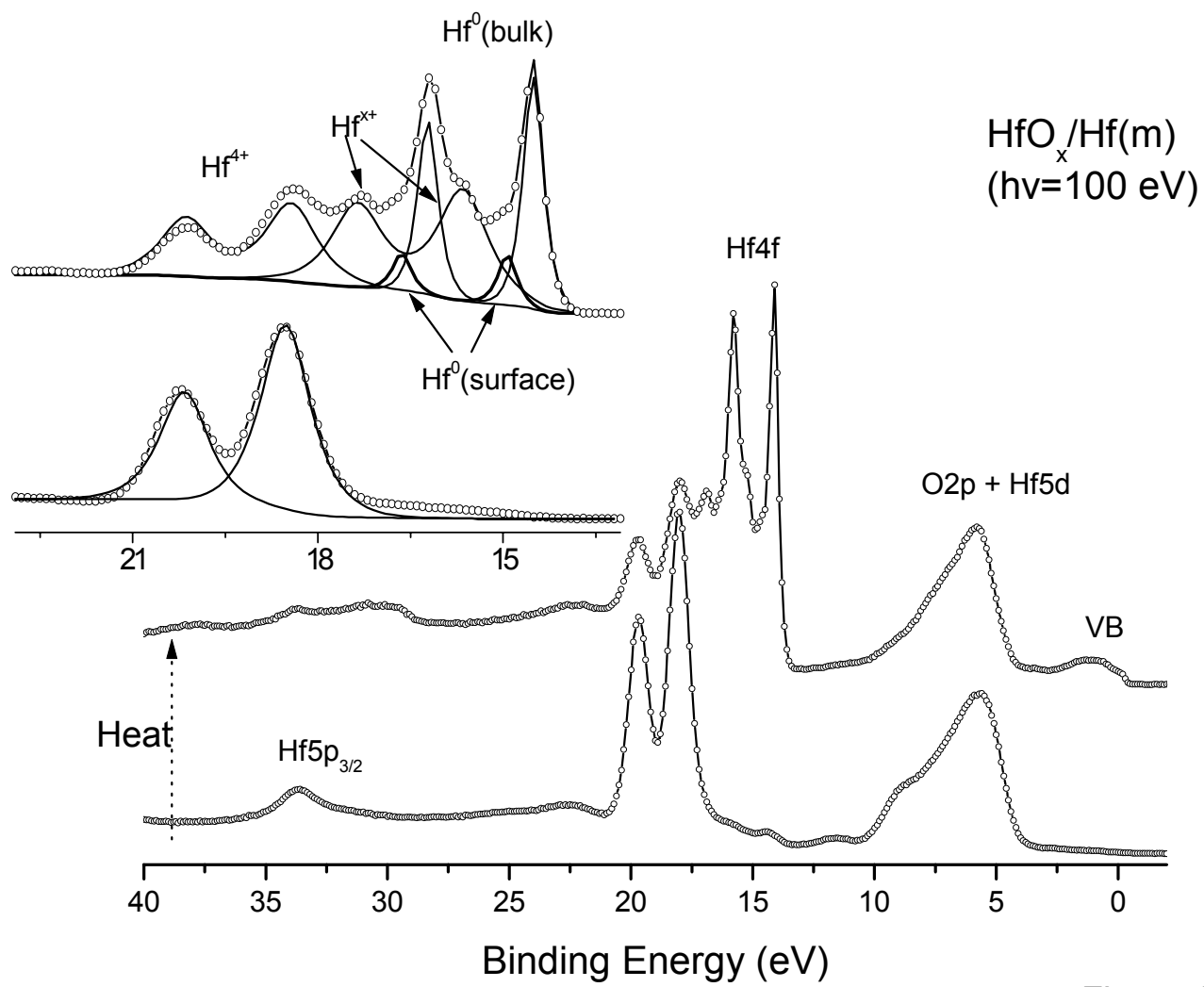


Figure 1

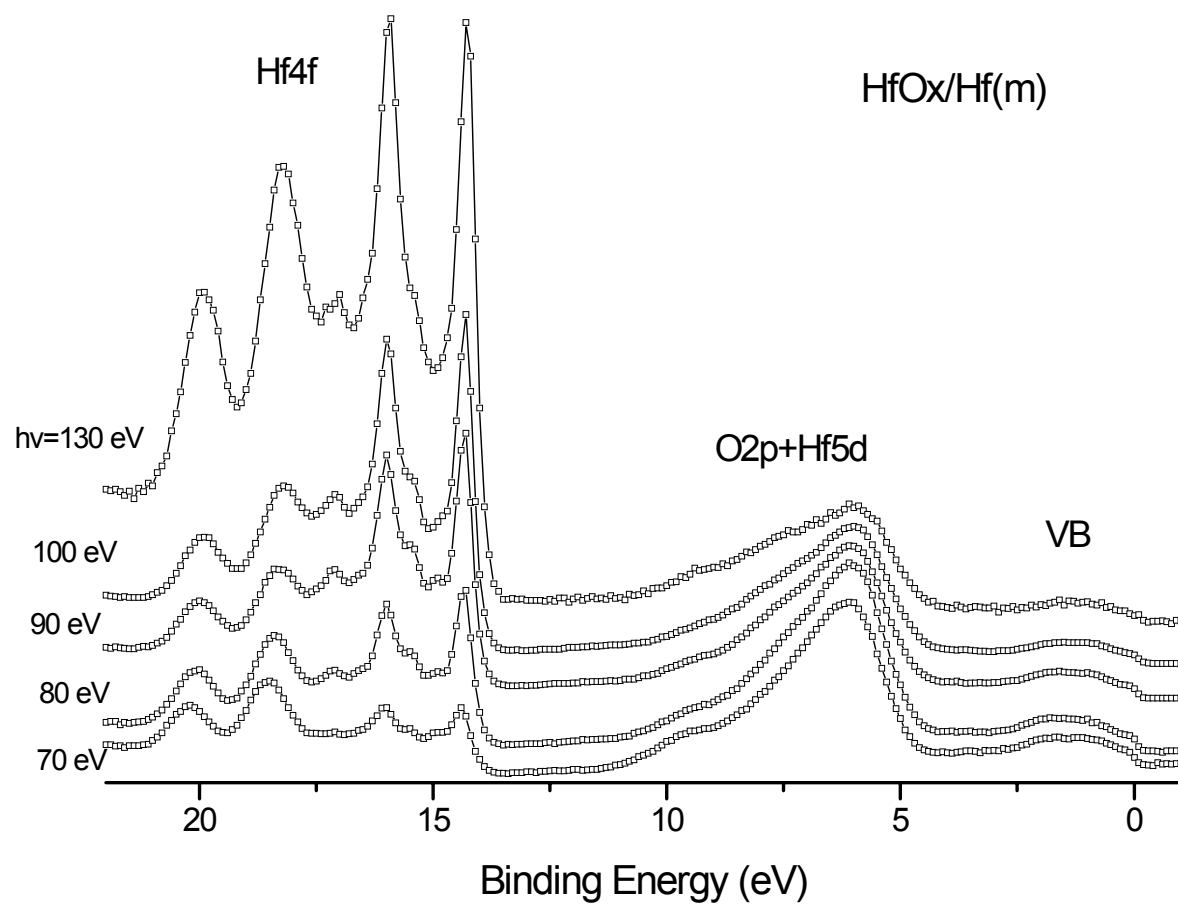


Figure 2

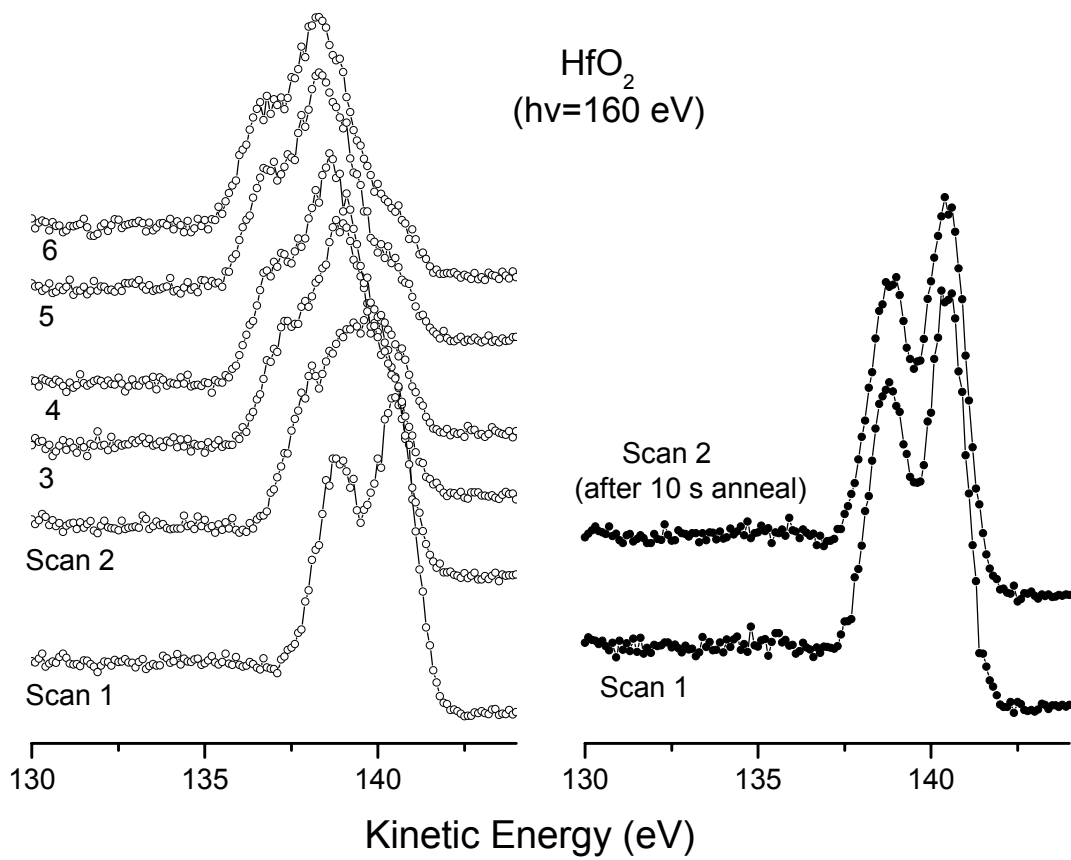


Figure 3

